

Water Rock Interaction [WRI 14]**Assessing initial conditions for chloride transport across low-permeability argillaceous rocks, Wellenberg, Switzerland**H.N. Waber^{a*}, M.Y. Hobbs^{a,b}, S.K. Frape^c^a*Rock-Water Interaction Group, Institute of Geological Sciences, University of Bern, Baltzerstrasse 1-3, 3012 Bern, Switzerland*^b*Nuclear Waste Management Organization (NWMO), 22 St. Clair Avenue East, M4T 2S3 Toronto, Ontario, Canada*^c*Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario, Canada***Abstract**

Information about fluid evolution and solute transport in a low-permeability metamorphic rock sequence has been obtained by comparing chloride concentrations and chlorine isotope ratios of pore water, groundwater, and fluid inclusions. The similarity of $\delta^{37}\text{Cl}$ values in fluid inclusions and groundwater suggests a closed-system evolution during the metamorphic overprint, and signatures established at this time appear to form the initial conditions for chloride transport after exhumation of the rock sequence.

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1. Introduction

Over the past decades, numerous investigations have examined solute transport across low-permeability rock formations considered as potential host rocks for the geological disposal of radioactive waste. One method for investigating solute transport is to numerically simulate natural tracer profiles that have developed with time in pore water residing in the connected pore space of the rocks. Such quantification requires knowledge of initial and boundary conditions over the time scale considered. The boundary conditions can be defined in part by the composition and evolution of groundwater sampled from water-conducting zones and/or regional aquifers surrounding the low-permeability rock sequence. Extrapolation into the past of such boundary conditions becomes less certain as the time period surpasses the residence time of sampled groundwater. Concerning the initial conditions in the low-permeability rock sequence, pore water tracer concentrations would ideally be defined at the time that exchange with surrounding groundwater commenced. In marine sediments, the original pore water is seawater. The composition of this original pore water is subjected to changes during burial, diagenetic, metamorphic

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and uplift events. The present study reports the assessment of such initial conditions for dissolved chloride in the metamorphic Palfris marl sequence at Wellenberg, Switzerland, based on its concentrations and isotope compositions in different fluid reservoirs, which are fluid inclusions, pore water, and groundwater.

2. Hydrogeological setting

The Wellenberg area constitutes low permeable marls with intercalated limestone layers (Palfris Formation s.l.) that were subjected to a low-temperature metamorphic overprint during Oligo-Miocene times [1]. Accumulation of the Palfris marl from its original thickness of about 200 m to presently at about 1000 m occurred during the emplacement of the Helvetic nappes during the late Alpine orogenic movements. The two oldest vein generations are deformed by later events and fully healed with ankerite or calcite, quartz and minor pyrite. A third calcite generation occurs together with quartz in healed or open, non-deformed veins. Fluid inclusions of Alpine vein quartz and calcite indicate maximum temperatures of about 200–250 °C, the presence of a two-phase $\text{CH}_4\text{-H}_2\text{O-NaCl}$ fluid with NaCl contents between 0.3 and 0.5 M [2], and a remarkably uniform gas composition [3]. Post-metamorphic uplift and erosion were accompanied with brittle (cataclastic) deformation, overprinting the pre-existing structural pattern and resulting in small amounts of syn- to post-cataclastic calcite and pyrite precipitated on the fracture walls.

Hydraulic conditions are hydrostatic in the Quaternary overburden and the upper Palfris Formation, sub-hydrostatic in the central, low-permeability Palfris Formation and artesian to hydrostatic in the sand-rich rocks of the Wissenberg-Firrenband Scholle and the Nordhelvetischer Flysch, respectively [1]. Groundwater is of a Ca-CO_3 to Na-HCO_3 chemical type with Cl^- contents up to 1.0 mmol/L and increasing residence times of <40 yrs in the Quaternary overburden and of <11 kyrs in the upper Palfris Formation. In the central Palfris Formation only small volumes of groundwater could be sampled before the reservoirs were exhausted. After correction for drilling fluid contamination, the Na-Cl type groundwater has a Cl^- content up to about 200 mmol/L; its residence time is not further quantifiable. Groundwater below the Palfris Formation is of a Na-HCO_3 type, poorly mineralised with Cl^- contents of 1.4–2.0 mmol/L and residence times >11kyrs [1].

3. Results

Concentration and isotope composition of chloride in fluid inclusions, pore water and groundwater were determined on archived material from the 1700 m long borehole SB1 drilled by Nagra at Wellenberg in 1990 [1]. In this borehole, the Palfris Formation (including minor Vitznau-Mergel and Schimberg-Schiefer) is composed of marls with average clay contents of 28 ± 11 wt.%. Rocks of the Wissenberg-Firrenband Scholle are more sand-rich with clay contents of about 11 ± 9 wt.%. Higher clay contents of 42 ± 17 wt.% occur in the rocks of the Nordhelvetischer Flysch and Mélange at the base of the borehole. The difference between total open porosities measured by Hg-injection (0.77–4.09 vol.%) and physical porosity obtained from density measurements (1.08–4.35 vol.%) is within the analytical uncertainty suggesting that in the investigated samples the volume of isolated pores (e.g. as fluid inclusions) is insignificant. The average total porosity is 2.44 ± 0.89 vol.% ($n=44$) for the Palfris Formation, 1.50 ± 0.51 vol.% ($n=3$) for the rocks of the Wissenberg-Firrenband Scholle and 1.05 ± 0.37 vol.% ($n=5$) for the rock of the Nordhelvetischer Flysch.

Chloride concentrations of the two Na-Cl type groundwaters from borehole SB1 are estimated to be about 152 and 165 mmol/L after correcting for drilling fluid contamination [1] with corresponding $\delta^{37}\text{Cl}$ values of +0.15‰ and +0.22 ‰ SMOC. Chloride concentrations of the Na-HCO_3 type groundwaters

located below the Palfris Formation s.l. are with increasing depth 1.41, 1.44 and 1.55 mmol/L [1] and corresponding $\delta^{37}\text{Cl}$ values are +0.71‰, +0.63‰ and +0.44‰ SMOC, respectively (Fig. 1).

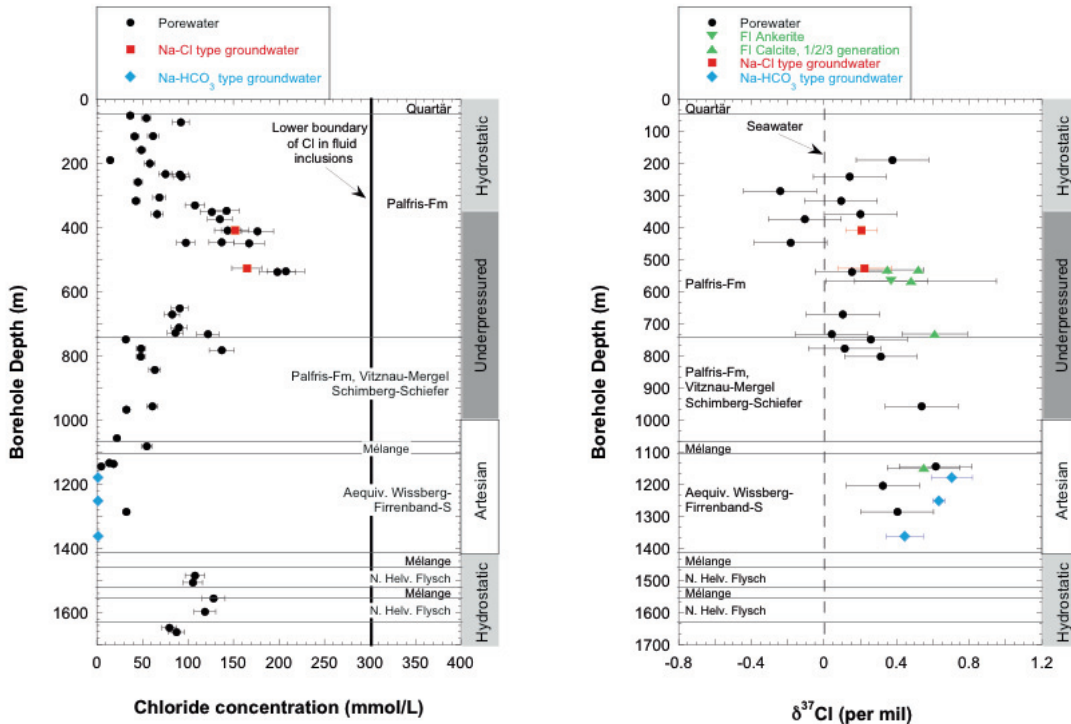


Fig. 1. Profiles of Cl^- concentrations and $\delta^{37}\text{Cl}$ signatures in pore waters, groundwaters, and fluid inclusions across the Palfris marls in borehole SB1 at Wellenberg, Switzerland.

Chloride concentrations extracted from the rock matrix by leaching range from 0.030–0.538 mmol/kg_{rock} at a solid–liquid ratio of 1. For the Palfris Formation, the fraction of the total porosity accessible to Cl^- was determined to be 0.33 based on Cl^- in Na-Cl type groundwater and Cl^- leached from rock samples nearby these groundwaters [4]. The same scaling of the total porosity was chosen for the rocks of the Nordhelvetischer Flysch, which have similar clay contents and compositions. In contrast, the Cl^- -accessible porosity was assumed to correspond to the total porosity in the clay-poor rocks of the Wissberg-Firrenband Scholle, which is supported by the low Cl^- concentrations measured in the relatively old groundwaters. Apparent pore water Cl^- concentrations in the Palfris Formation range from 15–208 mmol/L, those in the Wissberg-Firrenband Scholle from 13–32 mmol/L and those in the Nordhelvetischer Flysch from 80–128 mmol/L (Fig. 1). The corresponding ranges of $\delta^{37}\text{Cl}$ signatures are -0.11‰ – +0.54 ‰ SMOC in the Palfris Formation and 0.33–0.62‰ SMOC in the Wissberg-Firrenband Scholle.

Of the sixteen calcite samples prepared, only five contained sufficient Cl^- for isotope analyses. The $\delta^{37}\text{Cl}$ signatures vary between +0.35 to +0.61‰ SMOC with an average of $+0.50 \pm 0.1\%$ SMOC, which is less than the analytical precision of $\pm 0.15\%$. No distinction between ankerite and calcites, or between the different calcite generations is observed with respect to their measured $\delta^{37}\text{Cl}$ signatures (Fig. 1).

4. Evolution of porewater chloride and $\delta^{37}\text{Cl}$ signatures in the Palfris Formation

As a function of depth in borehole SB1 the pore water Cl^- concentration profile can be considered to consist of three broad zones (Fig. 1): i) An upper zone within the Palfris Formation to depths of

approximately 1080 m showing a broadly curved profile with a greater scatter in the lower limb where the sequence is more tectonised and maximum pore water Cl^- concentrations equal to those in Na-Cl type groundwater, but lower than minimum Cl concentrations in fluid inclusions; ii) an intermediate zone at depths from about 1080–1450 m corresponding to the Wissberg-Firrenband Scholle and with low pore water Cl^- concentrations in the range of those occurring in the Na- HCO_3 type groundwaters; and iii) lower zone down to 1670 m depth in the rocks of the Nordhelvetischer Flysch with higher pore water concentrations around 100 mmol/L.

The profile described by the pore water $\delta^{37}\text{Cl}$ signatures is almost a mirror image of the Cl^- concentrations with most positive values at the top and bottom of the Palfris Formation and lower values in the centre where highest Cl^- concentrations occur (Fig. 1). The concave shape of the profile seems significant in spite of the rather large cumulated uncertainty in $\delta^{37}\text{Cl}$ for the aqueous leach solutions. Most important, however, is the fact that the $\delta^{37}\text{Cl}$ values of fluid inclusions, groundwater and pore water from similar depth are identical within the cumulated uncertainty band. Although based on a limited dataset, similar observations are made for the zone below in the Wissberg-Firrenband Scholle.

The similarity of $\delta^{37}\text{Cl}$ signatures in fluid inclusions and groundwater suggests a common origin of chloride in these two reservoirs. A possible scenario for such common origin is a closed system evolution of the original pore water, which was seawater. Vein formation during diagenesis (ankerite) and metamorphic overprinting (calcite 1 to 3, quartz, and pyrite) occurred in relation with pressure solution processes. Membrane filtration of the original pore water during pressure solution and stylonite formation could potentially have led to fractionation and enrichment of ^{37}Cl in the fluid that precipitated calcite in veins and vugs. In turn, the bulk of the pore water in the rock matrix experienced only little, if any fractionation due to the large difference in water mass. Contemporaneously, the original pore water Cl^- concentration was diluted with water from the dehydration of clay minerals during the Alpine overprint resulting in fluid inclusion Cl^- contents slightly below that of seawater and late accumulations of Na-Cl groundwater in vugs with Cl^- contents only about a third of that of seawater. Such closed system evolution is also supported by independent chemical and isotopic data of the vein minerals and fluid inclusions [1, 2, 3]. It was not until the late stage cataclastic deformational phase that the system became locally open and fluid boiling occurred as indicated by the isotope composition of the rare calcite 4 [1].

The profile of present-day pore water Cl^- concentrations and $\delta^{37}\text{Cl}$ signatures appears to be the result of Cl transport out of the system. Driven by the chemical gradients established between pore water and surrounding groundwater, transport likely commenced after exhumation of the Palfris Formation. The decreasing Cl^- concentrations combined with the enriched $\delta^{37}\text{Cl}$ signatures towards top and bottom of the Palfris Formation suggest that this transport occurs mainly by diffusion. The initial conditions for such diffusion can thus be defined as corresponding to the Cl^- concentrations observed in Na-Cl groundwater and by the $\delta^{37}\text{Cl}$ signatures observed in Na-Cl groundwater and the fluid inclusions in the centre of the Palfris Formation and established during the late stages of the Alpine metamorphic overprint.

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